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Aggregation Numbers of Hydrophobic Microdomains Formed from Poly(dimethyldiallylammonium-*co*-methyl-*n*-dodecyldiallylammonium) Salts in Aqueous Solutions

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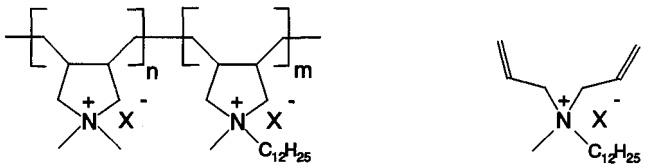
This paper provides a comparison of the solution properties in water of surfactants and polysoaps of closely related chemical structures. The main emphasis is placed on mean aggregation numbers (*N*) and how these values are affected by the nature of the counterions. The techniques used were steady-state fluorescence quenching and NMR spectroscopy. The aromatic counterions benzoate (Ben) and salicylate (Sal) bind very efficiently to micelles formed from methyl-*n*-dodecyldiallylammonium (MDDA) salts. ^{1}H NMR spectroscopic data show that these counterions are incorporated into the palisade layer, which most likely accounts for the observed efficiency of binding. Mean aggregation numbers of MDDA micelles with chloride, bromide, and benzoate counterions were determined using steady-state fluorescence quenching. It was found that *N* decreases in the order MDDAB ≈ MDDABen > MDDAC. The results for these micelles are of immediate relevance for understanding counterion effects on the formation of microdomains in aqueous solutions of the structurally related poly(dimethyldiallylammonium-*co*-methyl-*n*-dodecyldiallylammonium) salts, Copol C1-12 90/10 *X* (*X* = chloride, bromide, and benzoate). The ratio *n*/*m* indicates the relative amount of dimethyldiallylammonium monomer incorporated in the polymer relative to the methyl-*n*-dodecyldiallylammonium monomer. *N* values were measured for the microdomains formed from these polysoaps in aqueous solutions. Again, *N* decreases in the order Copol C1-12 90/10 Ben ≥ Br > Cl. Thus, evidence is provided that headgroup repulsion is a main factor which opposes growth of the microdomains. Addition of salt to Copol microdomains did not significantly influence the size of the domains. Interestingly, the mean aggregation number of Copol C1-12 *n*/*m* Cl microdomains did not change with an increasing number of *n*-dodecyl chains per polymer molecule when *n*/*m* > 98/2.

Key Words: **polysoaps; hydrophobic microdomains; micelles; counterion effects; aggregation numbers; fluorescence quenching.**

1. INTRODUCTION

Hydrophobically-modified water-soluble polyelectrolytes ("polysoaps") often aggregate in aqueous solutions to form micelle-like hydrophobic microdomains. In a previous paper, surface potentials of microdomains formed from poly(dimethyldiallylammonium-*co*-methyl-*n*-dodecyldiallylammonium) salts, Copol C1-12 90/10 *X*, were determined and compared with those of micelles formed from the corresponding methyldiallyl-*n*-dodecylammonium salts (Scheme 1) (1).



SCHEME 1

Herein, mean aggregation numbers (*N*) of Copol C1-12 *n*/*m* *X* (*n*/*m* = 99/1, 98/2, 96/4, and 90/10 for *X* = Cl, and *n*/*m* = 90/10 for *X* = Cl, Br, and benzoate (Ben)) (Scheme 1) are reported which provide further insights into the properties of these polysoap aggregates and the role of counterions in the aggregation process. The ratio *n*/*m* indicates the relative amount of dimethyldiallylammonium monomer incorporated in the polymer relative to the methyl-*n*-dodecyldiallylammonium (MDDA) monomer. The technique used for this purpose was steady-state fluorescence quenching. The basic idea underlying this method for determining aggregation numbers (2) is that in a system containing both fluorescent probe and quencher molecules, solubilized in an excess of micelles, the quenching will decrease with an increasing number of micelles because of a decreased probability of finding both the probe and the quencher molecule in the same micelle. If quenchers are distributed among micelles according to the Poisson - Boltzmann equation (3), then the probability of finding n quenchers associated with a given micelle is

$$P_n = [\langle Q \rangle^n / n!]\, e^{-\langle Q \rangle},$$

where $\langle Q \rangle$ is the average number of quenchers in the micelles, and [*M*] is the concentration of the micelles,

$$\langle Q \rangle = [Q]/[M].$$

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When we assume that fluorescence can be observed only for probes residing in micelles containing no quenchers at all, we write $I = P_0 I_0$, where I_0 is the intensity in the absence of quencher. It follows that

$$I/I_0 = e^{-\langle Q \rangle} .$$

Therefore, by plotting $\ln(I/I_0)$ vs $[Q]$, a straight line (going through the origin) with a slope of $[M]^{-1}$ should be observed (3). The mean aggregation number N can now be calculated, since $[M] = (C_D - \text{CMC})/N$, in which C_D is the total surfactant concentration.

The second technique that we employed was nuclear magnetic resonance. The hydrophobic counterions benzoate and salicylate (Sal) influence the local magnetic field in their direct neighborhood by the well-known aromatic ring current effect. This causes a change of the chemical shift of the surfactant CH_2 groups close to the head group upon micellization.

2. MATERIALS AND METHODS

The syntheses of the amphiphiles MDDA*X* and the polysoaps Copol C1-12 *n*/*m X* have been described in a previous paper (1). Since the molecular weight of Copol C1-12 90/10 Ben was determined to be 60,000-80,000, the number of monomeric units per polymer was calculated to be 240-320 (1). Pyrene (Aldrich, 99+%) and *N*-cetylpyridinium chloride (CPC, Merck AG, *pro analysi*) were used as received.

^{1}H NMR Spectra (200 MHz) were recorded with a Varian Gemini 200 instrument at ambient temperature. "Complexation-induced shifts" (CIS) of the hydrophobic counterions were determined as the chemical shift differences between MDDA*X* in D_2O at concentrations below and beyond the CMC, and as the chemical shift differences between Copol C1-12 90/10 Ben and Sal and Copol C1-12 90/10 bromide (in D_2O).

Pyrene fluorescence intensities in the presence of different quencher (CPC) concentrations were measured using an SLM SPF-500C spectrofluorometer equipped with a thermostated cell holder and a magnetic stirring device. The instrument settings were as follows: excitation wavelength, 335 nm; slit width, 2.5 nm. The emission spectrum was recorded from 360 to 410 nm (slit width, 0.5 nm, step size, 0.5 nm, filter 2). The quencher concentration $[Q]$ was varied by adding small (<10 *m*l) aliquots to the sample, while keeping the donor concentration constant (ca. 2×10^{-6} *M*). In all experiments, the surfactant concentration exceeded the CMC by 5 m*M*. Admittedly, the CACs of the surfactants are likely to be affected by the presence of the pyrene molecules, but since the probe will disturb all the (structurally similar) micelles in a similar way, the observed trends in the aggregation numbers as a function of the counterion are reliable. In the present approach the critical aggregation concentration (cac) of the polysoaps was assumed to be zero. To circumvent the problem of unacceptable inaccuracies of N resulting from considerable differences between the value of C_D and C_D - CMC, the polysoap concentration was chosen to be relatively high, viz., 50 m*M*.

Satisfactory duplicate results were obtained by exposing the solution to air with stirring for 15 min at the desired temperature at the beginning of each measurement. This ensured that the quenching effect of oxygen on the pyrene fluorescence intensity did not change during the experiment. The presence of oxygen did not change the relative intensities of the peaks in the pyrene fluorescence spectrum. The literature value (4) of the aggregation number of SDS, viz., 63 ± 1, could be satisfactorily reproduced. At every value of $[Q]$, the intensity I of the first vibronic peak of pyrene was measured. Since the ratio of I_1/I_3 did not measurably change during the experiment, no problems were encountered regarding the sensitivity of I_1 to the polarity of the environment that was sensed by the probe. From the slope of the linear plots of $\ln(I_0/I)$ vs $[Q]$, N could be calculated. In the case of polysoaps, N is expressed as the number of dodecyl chains per microdomain.

Finally, it has to be noted that the properties of some counterions induce specific problems. First, iodide is a very good quencher for pyrene, so that aggregation numbers of MDDAI micelles and Copol C1-12 90/10 I microdomains could not be obtained. Second, aggregates with salicylate counterions could not be studied because under the experimental conditions the counterion fluorescence was so strong in the spectral range studied that the pyrene fluorescence spectrum could not be resolved.

3. RESULTS AND DISCUSSION

3.1. Complexation-Induced Chemical Shifts

In a previous paper (1), we reported that salicylate, and to a lesser extent benzoate, counterions bind efficiently to micelles formed from methyl-*n*-dodecyldiallylammonium salts. We tentatively explained these observations by assuming that aromatic counterions associate strongly with micellar aggregates (5) because, being both hydrophobic and polarizable, they can be readily accommodated in the transition region between the hydrocarbon core and the external aqueous phase. If the boundary between these two regions is rather sharp (5), the large binding efficiency of salicylate may be caused by the ability of the *o*-hydroxyl group to infiltrate the aqueous phase by forming hydrogen bonds, so that this ion perfectly fits into the palisade layer. These proposals can be tested since it is possible to determine the position of the hydrophobic counterions at the micellar binding sites using ^{1}H NMR spectroscopy on the basis of the magnetic anisotropy effect of the aromatic ring current. Therefore, complexation will be manifested in a chemical shift difference between ^{1}H NMR signals of chemically iden-

TABLE 1
CIS Values for MDDA*X* Micelles[a]

Peak[a]	MDDAC1 *d* (ppm)	MDDABr *d* (ppm)	MDDAI *d* (ppm)	MDDASal *d* (ppm)	MDDABen *d* (ppm)	MDDASal CIS (ppm)[b]	MDDABen CIS (ppm)[b]
a	3.26	3.35	3.37	2.82	2.76	0.51 ± 0.07	0.57 ± 0.07
b	1.84	1.90	1.89	1.39	1.40	0.49 ± 0.04	0.48 ± 0.04
c[d]	1.33	1.37	1.32	1.39	1.40	≈0	≈0
d	0.94	0.96	0.92	1.01	1.03	-0.07 ± 0.02	-0.09 ± 0.02
e	3.10	3.15	3.12	2.82	2.81	0.30 ± 0.02	0.31 ± 0.02
f	4.03	3.90	4.09	3.67	3.67	0.33 ± 0.10	0.33 ± 0.10
g	6.10	6.15	6.14	5.76	5.80	0.37 ± 0.03	0.33 ± 0.03
h	5.81	5.82	5.79	5.57	5.56	0.24 ± 0.02	0.25 ± 0.02

Chemical shifts of the aromatic couterions

	Free Sal	Free Ben	Bound Sal	Bound Ben	Salicylate CIS (ppm)[c]	Benzoate CIS (ppm)[c]
i		7.49		7.32		0.17
j		7.86		7.97		-0.11
k		7.49		7.32		0.17
l	7.79		7.80		≈0	
m	7.46		7.20		0.26	
n, o	6.96		6.75		0.20	

[a] The structural assignment of the signals in MDDA*X* spectra is shown in Fig. 1. For the hydrophobic counterions the assignments follow (as an example, *o*-COO^-, *m*-OH means that the ^1H nucleus is in an *ortho* position relative to the carboxylate group and in a *meta* position relative to the hydroxyl substituent). Benzoate: i, *m*-COO^-, and k, *p*-COO^- (one signal); j, *o*-COO^-. Salicylate: 1, *o*-COO^-, *m*-OH; m, *p*-COO^-, *m*-OH; n and o, *m*-COO^-, *o*- and *p*-OH (one signal).

[b] Complexation-induced shift relative to the mean shift of the MDDAHalide peaks.

[c] Complexation-induced shift relative to the free hydrophobic counterion. The error equals the inaccuracy in determining the chemical shift difference (≈0.01 ppm).

[d] Long-chain CH_2 moiety; these nine CH_2 groups have approximately the same chemical shift.

tical hydrogen atoms in micelles and in monomeric surfactants. These complexation-induced shifts of the ^1H resonances of the micellar aggregates (relative to MDDAHal resonances) are listed in Table 1. Figure 1 shows the assignment of the ^1H NMR resonances of the surfactant in the micelle.

The shifts are largest near the headgroups, indicating that the hydrophobic counterions are located in this area. This provides evidence for a hydrophobic component to the binding of the salicylate and benzoate anions to the micellar surface. Unfortunately, the results do not provide compelling evidence for the "salicylate fit hypothesis."

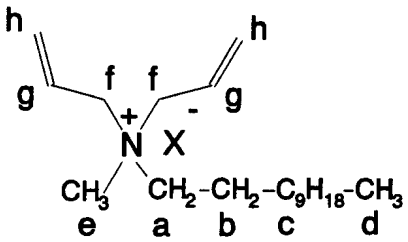

FIG. 1. Structural assignment of the ^1H NMR peaks of the methyldodecyldiallylammonium moiety of MDDA*X*. The letter c comprises nine CH_2 groups in the dodecyl chain having overlapping ^1H NMR resonances: c_{11} corresponds to the CH_2 group closest to the long-chain terminal methyl group, and c_3 resides closest to the headgroup.

Similar data for Copol microdomains are listed in Table 2. The NMR peaks are now assigned by capital letters but the locations of the corresponding hydrogen atoms are comparable to those indicated in Fig. 1. The shielding effects are less pronounced than those for the micelles. In the compact coils of the polysoaps, counterions cannot reside in between two "headgroups" because these are covalently linked; presumably the polymer backbone is wrapped around the counterions so that the effects of the aromatic ring current appear to be "distributed" among all parts of the microdomains.

All results are graphically depicted in Fig. 2, where the shifts of the ^1H NMR micelle resonances are plotted as a function of the distance relative to the ammonium headgroup.

3.2. Aggregation Numbers

The analysis of the steady-state quenching data, as presented in the Introduction, seems very simple at first sight. Unfortunately, there may be pitfalls in the determination of absolute values of *N* using this method (6). First, there is the problem of finite quenching rates, inherent to the steady state-method and always leading to experimental values of

TABLE 2
CIS Values of Copol C1-12 90/10 Sal and Copol C1-12 90/10 Ben

Peak[a]	Copol C1-12 90/10 halide *d* (ppm)	Copol C1-12 90/10 salicylate *d* (ppm)	Copol C1-12 90/10 benzoate *d* (ppm)	CIS Sal *d* (ppm)	CIS Ben *d* (ppm)
A	3.27	3.16	3.17	0.11	0.10
B	1.55	1.36	1.39	0.19	0.16
C[b]	1.30	1.16	1.24	0.14	0.14
D	0.88	0.86	0.85	0.02	0.03
E	3.15	3.03	3.05	0.12	0.10
F	3.83	3.67	3.71	0.16	0.12
G1[c]	2.72	2.48	2.55	0.24	0.17
G2[d]	2.31	2.10	2.15	0.22	0.16
H[e]	1.55	1.36	1.39	0.19	0.16
Ben1	7.49		7.47		0.02
Ben2	7.86		7.88		-0.02
Sal1	6.96	6.91		0.05	
Sal2	7.46	7.38		0.08	
Sal3	7.79	7.83		-0.04	

[a] For structural assignments see Fig. 1.
[b] Long-chain CH_2 (eight overlapping peaks).
[c] *Cis tert*-ring C*H*.
[d] *Trans tert*-ring C*H*.
[e] Could not be resolved from peak B.

N that are too low. Second, several so-called Turro-Yekta fluorescence analyses have been performed using the assumption that the aggregates are monodisperse. However, it appears that polydispersity can seriously affect the results although this possibility is not readily reflected by deviations from linearity in plots of $\ln(I/I_0)$ vs $[Q]$. Therefore, we contend that the aggregation numbers obtained in the present study are not necessarily absolute values. However, trends are expected to be reproduced honestly, at least for microdomains formed from Copol C1-12 90/10 *X*, all of which possess molecular weights having the same polydispersity (since they were prepared from the same supply of Copol C1-12 90/10 Cl).

When applying the steady-state model, both the donor and the quencher should reside exclusively in the micellar or polysoap aggregates. The choice of the quencher for the cationic systems under investigation is not straightforward. For anionic SDS micelles, the donor-quencher pair 9-methylanthracene/ruthenium bipyridyl has been frequently employed (4). But this quencher will most probably be repelled from the surface of cationic assemblies so that another quencher had to be chosen. One could consider a neutral (or even anionic) quencher to preclude electrostatic repulsions. However, in measurements of aggregation numbers of neutral polysoaps, Zdanowicz and Strauss (7) encountered serious problems when using the uncharged benzophenone as a quencher for pyrene, because it was even solubilized in nonmicellized portions of the polymer so that the observed aggregation numbers were independent of the extent of micellization. The choice of a cationic quencher which binds efficiently to cationic aggregates solely via hydrophobic interactions would prevent this problem because it will not bind to nonaggregated (nonhydrophobic) portions of the polymer.

Geetha *et al.* (8) recently obtained satisfactory results using 8-anilino-1-naphthalenesulfonic acid as a donor and *N*-cetylpyridinium chloride as a quencher for Turro-Yekta studies of a neutral macromonomer. However, we had previously encountered complexities when using an anionic dye (methyl orange) to probe cationic micelles and microdomains because of specific dye-induced aggregation (9). Therefore, we preferred to employ a neutral, hydrophobic donor. The donor/quencher pair pyrene/*N*-cetylpyridinium chloride, recommended in the literature (10), was expected to be compatible with the assemblies under investigation, particularly since Gamboa and Olea (11) have recently shown that CPC binds very efficiently to cetyltrimethylammonium bromide (CTAB) micelles.

"Relative" aggregation numbers of MDDA*X* micelles and of Copol C1-12 *n*/*m X* microdomains are summarized in Table 3. These values can be directly compared, taking into account the problems mentioned above. The aggregation numbers of microdomains formed from Copol C1-12 90/10 Br and Ben as a function of the concentration of added salt are listed in Table 4. For the MDDA*X* micelles and Copol C1-12 90/10 Hal microdomains, the effect of headgroup repulsion lowering the aggregation tendency is indicated by $N(X = \text{Br}) > N(X = \text{Cl})$. Based on previous studies by Underwood and Anacker (5), and anticipated on electrostatic grounds, one would anticipate that the aggregation number of MDDABen will exceed that of MDDABr, as was indeed borne out in practice for the Copol microdomains.

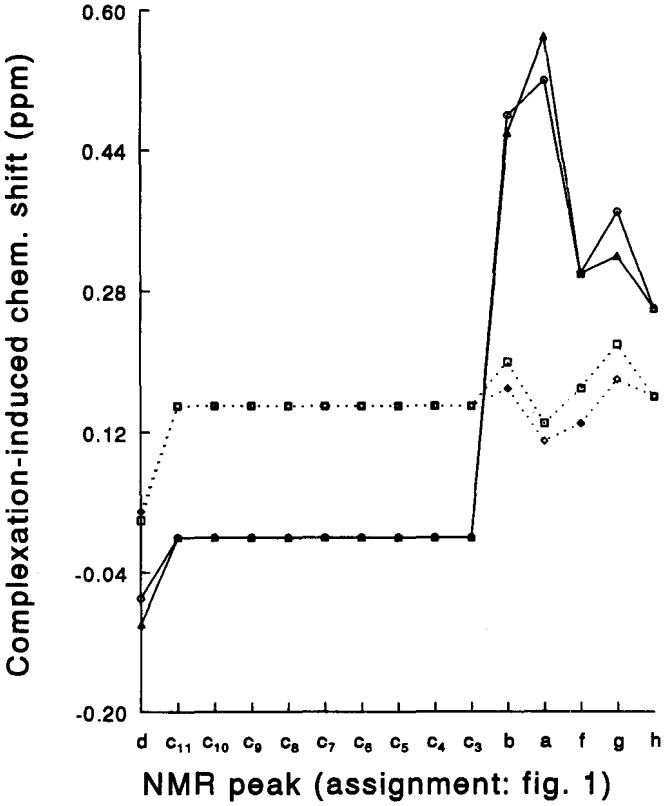

FIG. 2. Complexation-induced shifts of micellar MDDA$^+$ and polysoap microdomain ^{1}H NMR resonances in the presence of benzoate and salicylate counterions. Δ, MMDABen; ❍, MMDASal; ◊, Copol Ben; ❑, Copol Sal.

From the observation that the wavelength of maximum absorption of the solvatochromic dye methyl orange only changed in the presence of Copol C1-12 96/4 or 90/10, we infer that formation of *hydrophobic* microdomains only takes place when the ratio *n*/*m* exceeds 96/4 (12). Thus, the extent of micellization indeed varies with *n*/*m*. The extent of intra- or intermolecular micellization does, however, not greatly affect the apparent aggregation number of the microdomains as evidenced by the trends observed among the Copol C1-12 *n*/*m* Cl systems. Zdanowicz and Strauss (7) ascribed this result to stacking of the quencher to nonaggregated polymer chains. In the case of our cationic quencher this appears to be highly improbable (*vide supra*), but donor-induced aggregation cannot be rigorously excluded.

TABLE 3
Aggregation Numbers of MDDA*X* Micelles and Copol C1-12 *n*/*m* *X* Microdomains at 25 ± 0.1°C

Compound	*N*
MDDACl	31 ± 1
MDDABr	39 ± 1
MDDABen	37 ± 1
Copol C1-12 99/1 Cl	5 ± 1
Copol C1-12 98/2 Cl	10 ± 1
Copol C1-12 96/4 Cl	10 ± 1
Copol C1-12 90/10 Cl	10 ± 1
Copol C1-12 90/10 Br	24 ± 1 (19 ± 1)[a]
Copol C1-12 90/10 Ben	29 ± 1 (23 ± 1)[a]

[a] Corrected value based upon a critical aggregation concentration of 10 m*M* (see text).

TABLE 4
Aggregation Numbers of Copol C1-12 90/10 *X* as a Function of Added Na*X* at 25 ± 0.1°C

[Added Na*X*] (m*M*)	N^a (*X* = Br)	N^a (*X* = Ben)
0	24 ± 1	29 ± 1
50	22 ± 1	29 ± 1
100	21 ± 1	25 ± 1
200	21 ± 1	24.0 ± 1

[a] Expressed as the number of dodecyl groups per microdomain.

There is ample literature precedent that addition of salt increases the aggregation number of ordinary micelles by increasing the degree of counterion binding and diminishing headgroup repulsions (13). As becomes apparent from the data in Table 4, this opposes the trend observed for the Copol microdomains. However, we have to bear in mind that critical aggregation concentrations were neglected in the calculation of *N*. As we have shown previously (1), there is strong evidence that Copol C1-12 90/10 Ben and Br have a CAC of ca. 10 m*M*. By using this value in the calculation of *N*, we find mean aggregation numbers of 23 and 19, respectively. These values are very similar to the aggregation numbers of microdomains formed by Copol C1-12 90/10 Br and Ben in a concentrated salt solution (200 m*M*). Thus, the observed reduction of *N* in the presence of added salt may well be explained by a decrease of the critical aggregation concentration of the polysoap (the real aggregation number may even remain unchanged). This phenomenon is commonly found for ordinary micelles, where addition of inert electrolytes lowers the electrostatic repulsion between the headgroups through increased counterion binding.

However, the assumption of *N* remaining constant may be contrasted with results of studies of ordinary micellar systems. Recently, Reekmans *et al.* (14) have shown that upon adding salt, "mature" micelles in fact do not grow; it is solely the premicellar aggregates and small micelles that become larger. Thus, the apparent increase of *N* upon adding salt is ascribed to a reduction of the polydispersity of the size of the aggregate. One could even assume that the absence of polydispersity of Copol microdomain size might offer a tentative explanation for the observed invariance of *N* with [added salt], but this suggestion needs further confirmation.

4. CONCLUSIONS

Hydrophobic counterions can penetrate into the palisade layer of micelles formed from MDDA*X*. This is impossible

in the case of the structurally related polysoaps Copol C1-12 90/10 *X*, where the headgroups are covalently linked.

The aggregation behavior of the polysoaps Copol C1-12 90/10 *X* depends on surface electrostatic effects in a similar way as micellization depends on headgroup repulsion forces.

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